

Using Q-XAS to Determine Zinc Speciation in a Contaminated Environment

Samuel M. Webb and Jean-François Gaillard

Department of Civil Engineering, Northwestern University, 2145 Sheridan Road, Evanston, IL, 60208-3109, USA

Introduction

Metal smelting operations have introduced large concentrations of metals in aquatic systems [1]. In order to understand the fate of these metals, one needs to assess the mobility, the reactivity, and the toxicity of these contaminants in the impacted environment. Hence, the determination of the chemical speciation of metals becomes an essential issue. Often, this is achieved by means of selective extraction procedures or by performing equilibrium calculations coupled to appropriate surface complexation models [2]. However, these approaches can be misleading because wet chemical methods are operationally defined and natural systems are quite frequently out of equilibrium [3]. In addition, biological systems have evolved a variety of mechanisms to respond to metal stress, some of which involve a re-speciation of the metals [4-6], and that are not yet well understood. Therefore, there is a need to develop speciation schemes that allow ones to determine directly the various chemical and physical forms of the metals in the environment. In a previous paper [7] we investigated the speciation of zinc in contaminated sediments using analytical electron microscopy (AEM). Zinc bearing particles ranged from near spherical colloids to small grains intimately associated either with biological templates or as separate amorphous entities. Elemental analyses showed that zinc was present in structures composed of iron and phosphorus close to the source of contamination, whereas further away zinc was primarily associated with sulfur. We present here an approach to quantifying the chemical speciation of Zn by Q-XAS.

Methods and Materials

Sample Collection and Preparation

Three sampling sites were chosen along a gradient of contamination in Lake DePue, IL, a backwater lake on the Illinois River. These sites are described in details in Webb, et. al. [7]. Briefly, the first site, C₁, is located in a highly contaminated, shallow stream which drains into the lake. Zinc concentrations are approximately 300 μM in the stream and up to 30% by dry weight in the sediments. The stream flows in Lake DePue at site C₂. The site has a deltaic sedimentation pattern and total zinc ranges from 2 to 10% by dry weight. The last sediment collection site, M₁, is located away from the bulk of the zinc contamination, in the middle of the lake. Zinc concentrations in these sediments are close to background levels (~ 100 ppm) except for the upper 1 cm of freshly sedimented material which contains up to 0.5% zinc. Sediment samples were collected with a piston corer, sub-sampled at 2 cm intervals, placed in between Kapton tape, and immediately placed into liquid N₂ to block any chemical reaction until analyzed.

Experimental

X-ray Absorption measurements were performed on the DND-CAT bending magnet beamline. A detailed description of the Q-XAS experimental setup can be found in Quintana [8]. A Si(111) double crystal monochromator was used to vary the X-ray energy from 200 eV below to 750 eV above the absorption K

edge of Zn (9659 eV). The incident intensity, I_0 , and transmitted intensity, I_T , were measured by appropriately positioned ionization chambers. The fluorescence signal I_F , was measured with a Lytle detector equipped with a Cu filter. The Lytle cell and the ionization chambers were continuously sampled at a 12.5 kHz using a sixteen-bit analog to digital converter. Ten successive scans of 75 seconds each were recorded for each sample.

Data Analysis

The QXAS analysis is described in more details in [9]. Briefly, it consists in determining the various proportions of the different metal coordination shells based on a selected set of standard spectra. Since the Q-XAS mode allows one to obtain experimental errors, we use a pseudo-Monte Carlo method to carry over errors through all calculations. The errors for the normalization of the spectra and isolation of the EXAFS region were obtained after conventional curve fittings procedures and using AUTOBK [10]. The process was calibrated by determining the composition of known mechanical mixtures using a non-negative least square fit of the EXAFS signals. Standards were chosen after a careful geochemical analysis of Lake DePue sediments [7]. Standards included ZnS, ZnO, Zn(OH)₂, ZnCO₃, zinc phosphate (Zn₃(PO₄)₂), and hydrozincite (Zn₃CO₃(OH)₄).

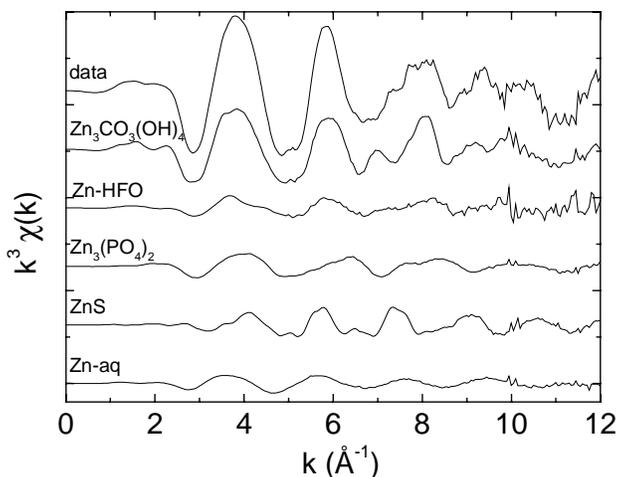
Results and Discussion

Figure 1 shows the raw unfiltered EXAFS spectrum of a sediment sample, and the different components that explain this spectrum. In this sample, the major species of Zn present included Zn₃CO₃(OH)₄, ZnS, Zn₃(PO₄)₂, hydrated Zn, and Zn associated with iron oxides. The amplitude of each of the components is shown proportional to its respective contribution to the total signal of the sample.

Figure 2 provides the major zinc species calculated as percent of the total zinc measured by atomic spectroscopy. Site C₁ (Fig. 2a) shows a large proportion of hydrated zinc, *i.e.*, a zinc coordination shell that is indistinguishable from the one of the aqueous ion, throughout the sampled core (25-40%) as well as a high concentration of hydrozincite below 5 cm. This suggests that a large portion of the zinc at this site is relatively labile and easily transportable. Additionally, the zinc tied up in iron oxides and in phosphates are strongly correlated over most of the core. The characterization of these sediments by AEM [7] has shown that a significant fraction of the zinc containing colloidal matter present is composed of iron-zinc-phosphates.

Sediment Q-XAS results from the deltaic site, C₂, are shown in Fig. 2b. The most striking feature in the speciation of zinc at this location is the cyclical nature of the Zn₃(PO₄)₂ coordination shell.

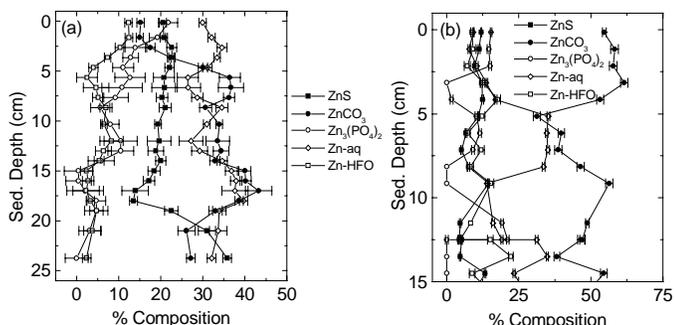
Figure 1



The relative concentration of zinc phosphates oscillates between nearly absent to about 15% with a period of about 4-5 cm. Since the sedimentation rate has been measured to be about 3-4 cm yr⁻¹ (54), this suggests that flooding events may be accompanied with metal contamination peaks. The Q-XAS speciation calculated at M₁ (not shown) is dominated almost entirely by ZnS. In addition, hydrated zinc is nearly absent at this site.

The amount of zinc present in the sediments and the water column decreases rapidly between the three sites. When Zn is present at high concentrations, its chemical speciation is dominated by species that are labile, e.g., hydrated zinc and carbonates, and therefore Zn is more mobile. In opposition, at site M₁ little zinc is present and it is present under the form of a rather inert zinc-sulfide. Previous work [11] has shown that ZnS oxidation is kinetically hindered. Hence, even if these sediments were to be resuspended, they may not release any significant amounts of Zn. This explains the lack of significant zinc contamination in the far reaches of the lake.

Figure 2



Acknowledgments

This work was supported by NSF Grant # MCB-9807697, and was performed at the DuPont-Northwestern-Dow Collaborative Access Team (DND-CAT) Synchrotron Research Center, Sector 5, Advanced Photon Source. DND-CAT is supported by the E.I. DuPont de Nemours & Co., the Dow Chemical Company, the NSF through Grant DMR-9304725, and the State of Illinois through the Department of Commerce and the Board of Higher Education Grant IBHE HECA NWU 96. Use of the Advanced Photon Source was supported by the U.S. Department of Energy, Basic Energy Sciences, Office of Energy Research under Contract No. W-31-102-Eng-38.

References

- [1] Nriagu J. O. "Environmental Impacts of Smelters", in *Advances in Environmental Science and Technology*, Vol. 15 (ed. J. O. Nriagu), pp. 608, John Wiley (1984).
- [2] Westall J. C., Zachara J. L., and Morel F. M. M., "MINEQL, a Computer Program for the Calculation of Chemical Equilibrium Composition of Aqueous Systems", Parsons Laboratory, MIT (1976)
- [3] Brezonik P. L., *Chemical Kinetics and Process Dynamics in Aquatic Systems*, Lewis (1994)
- [4] Beveridge T. J., Doyle R. J., *Metal Ions and Bacteria*, John Wiley (1989)
- [5] Silver S., "The bacterial view of the periodic table: specific functions for all elements", in *Geomicrobiology: Interactions between microbes and minerals*, Vol. 35 (ed. J. F. Banfield and K. H. Nealson), pp. 345, Mineralogical Society of America (1997)
- [6] Silver S. and Phung L. T., "Bacterial heavy metal resistance: New surprises", *Annu. Rev. Microbiol.* (50), 753, (1996)
- [7] Webb S. M., Leppard G. G., and Gaillard J.-F., "Zinc speciation in a contaminated aquatic environment: Characterization of environmental particles by analytical electron microscopy" *Environ. Sci. & Technol.*, in press (2000)
- [8] Quintana J. P. Q., "Uncertainty Determination in QXAFS Measurements", in press, (2000)
- [9] Gaillard J.-F., Webb S. M., "Direct Determination of Metal Speciation by Q-XAS", to be submitted to *Anal. Chem.*
- [10] Newville M., Livins P., Yacoby Y., Stern E. A., Rehr J. J., "Near-edge x-ray-absorption fine structure of Pb: A comparison of theory and experiment", *Phys. Rev. B* (47), 14126-14131 (1993).
- [11] Rimstidt J. D., Cermak J. A., and Gagen P. M., "Rates of reaction of galena, sphalerite, chalcopyrite, and arsenopyrite with Fe(III) in acidic solutions" in *Environmental geochemistry of sulfide oxidation* (ed. C. N. Alpers and D. W. Blowes), pp. 2-13, Am. Chem. Soc. (1994)